

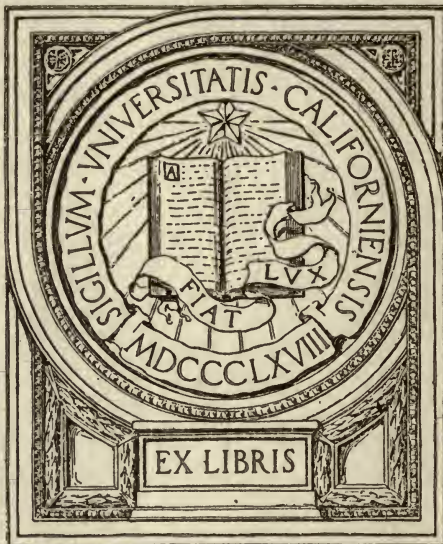
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The Role of Ionic Activities in Catalysis in Liquid Systems

Acetyl-Chloramino-Benzene \longrightarrow P. Chloracetanilide

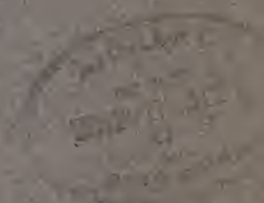
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A THESIS

PRESENTED TO THE GRADUATE SCHOOL AS PARTIAL
FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY.

BY

HARRY SELTZ



Philadelphia, Pennsylvania
1922

UNIV. OF
PENNSYLVANIA

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ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Dr. Herbert S. Harned, under whose direction and guidance this work was done.

Exchange

INTRODUCTION

The catalytic effect of specific ions on the velocities of certain reactions, in liquid systems, has been the subjects of much investigation. The velocity of hydrolysis of esters and the inversion of sucrose are accelerated by the presence of either the hydrogen or hydroxyl ions. Benzaldehyde is converted to benzoin by the catalytic influence of the cyanide ion. Hydrogen peroxide decomposes into water and oxygen upon the introduction of the iodine ion. Acetyl-chloramino-benzene is converted to p-chloracetanilide by the simultaneous presence of the hydrogen and chlorine ions.

It was early noticed that, in very dilute solutions, the velocities of such reactions were proportional to the concentrations of the catalyzing ions, as computed from conductivity ratios, a relation which would be predicted by the classic "Dissociation Theory." As the concentration of the catalyzing ion increases, however, this proportionality no longer holds. The velocity increases more rapidly than would be expected from conductivity measurements. To explain this discrepancy the "Dual Theory" of catalysis was advanced by Senter (*Trans. Chem. Soc.* 91, 467, 1907); Acree (*Amer. Chem. Journ.* 37, 410; *ibid.* 38, 258, 1907); and others. This theory attributed a catalytic effect not only to the ion in question, but also to the undissociated molecule. For example, in the hydrolysis of esters by hydrochloric acid if we denote the catalytic effect of the undissociated molecule of the acid by k_m , and that of the hydrogen ion by k_h , and the total observed velocity constant by k , then:—

$$k = \alpha k_h + (1 - \alpha) k_m$$

in which α is the degree of dissociation of the acid at the given concentration. This theory has considerable applicability, but there is no experimental evidence to prove the existence of any such catalytic property of the undissociated molecule.

Arrhenius, as early as 1899, indicated a possible relation between the osmotic pressures of the ions and their catalytic influence on certain reactions. Apparently the first suggestion

that the ion activities, as defined by G. N. Lewis (Proc. Amer. Acad. 37, 49 (1901), etc.), should be used in velocity calculations in catalysis in liquid systems, was made by Harned (J. Amer. Chem. Soc., Vol. 37, 11, 2460 (1915)). Such a conclusion can be reached from thermodynamic considerations.

The "Free Energy Function" (F) is defined by the following equation:—

$$F = U - TS + PV \dots \dots \dots (1)$$

in which, U = Internal Energy

T = Absolute Temperature

S = Entropy

P = Pressure

V = Volume

The differential equation relating these quantities, pressure and temperature constant, is:—

$$dF_{P,T} = dU - TdS + PdV \dots \dots \dots (2)$$

For a reversible process the following relation exists between the entropy, internal energy, and work (W),

$$dS = \frac{dU + W}{T} \dots \dots \dots (3)$$

Substituting this value of dS in equation (2):—

$$[-dF]_{P,T} = W - PdV \dots \dots \dots (4)$$

for any reversible process.

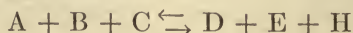
The thermodynamic criterion, therefore, for equilibrium in any system where only mechanical work is done, is that:—

$$dF = 0$$

The "activity" (a) of any component of a system is related to the free energy of that component by the equation (G. N. Lewis, Proc. Amer. Acad. Art. Sci. 43, 259 (1907); Bornsted, J. Am. Chem. Soc. 42, 761 (1920)) :—

$$F = RT \ln a + i \dots \dots \dots (5)$$

in which "i" is the free energy at some zero state. Let us consider the following reaction:—



in which A, B, C, D, E and H represent molal quantities. Let

F_A, F_B, F_C —etc., represent the corresponding free energies. Then, for equilibrium ($dF = 0$):—

$$F_A + F_B + F_C \times F_D + F_E + F_H$$

or, from equation (5):—

$$(RT \ln a_A + i_A) + (RT \ln a_B + i_B) + (RT \ln a_C + i_C) = (RT \ln a_D + i_D) + (RT \ln a_E + i_E) + (RT \ln a_H + i_H)$$

and,

$$\ln a_D + \ln a_E + \ln a_H - \ln a_A - \ln a_B - \ln a_C = \frac{\Sigma i}{RT} = K_1$$

$$\text{or, } \frac{a_D \times a_E \times a_H}{a_A \times a_B \times a_C} = K \dots\dots\dots (6)$$

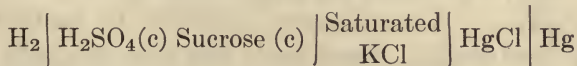
We thus arrive at an expression for equilibrium similar in form to the "Mass Action Law," except that the usual concentrations are replaced by activities. This is the thermodynamic expression for equilibrium in any system. If we consider this equilibrium to be a dynamic one, the opposing velocities being equal, it follows that the velocities can be related:

$$\left. \begin{aligned} V &= K a_A \times a_B \times a_C \\ V' &= K a_D \times a_E \times a_H \end{aligned} \right\} \dots\dots\dots (7)$$

Such a deduction leads directly to the idea that, in the consideration of reaction velocities, catalyzed by specific ions, the proportionality is not to the concentrations of such ions, but rather to their activities.

Harned (J. Amer. Chem. Soc., Vol. XL, 1461 (1918)), in a discussion of catalysis in the presence of neutral salts, pointed out some interesting relations between reaction velocities and activities.

Jones and Lewis (J. of Chem. Soc. 117, 1120 (1920)), studied the inversion of sucrose by sulphuric acid from the view point of the activity of the catalyzing hydrogen ion. They calculated this activity, in the presence of various concentrations of sucrose, from electromotive force measurements of the cells:—



They found that the reaction could be explained on the basis of the hydrogen ion activity, providing the "water displacement

effect" be taken into consideration. They obtained good agreement for K_{bl} from the relation:—

$$K_{bl} = \frac{K_{uni}}{[H_2O] \times a_H}$$

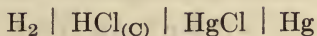
in which K_{bl} is the true bimolecular velocity constant at any temperature, K_{uni} the observed unimolecular constant, $[H_2O]$ the concentration of the water, and a_H the activity of the hydrogen ion. The objection to this work is the fact that the calculation of the hydrogen ion activities from the cell indicated above, requires the elimination of the liquid junction potential by saturated potassium chloride solution. Furthermore, in this reaction the water molecule enters into the stoichiometrical equation, introducing a complicating factor.

Åkerlof (Z. physik. Chem. 98, 260 (1921)) has carried out an extensive investigation of the hydrolysis of ethyl acetate by acids in the presence of neutral salts; with corresponding measurements of hydrogen ion activities. Here again the liquid junction difficulty enters. Moreover, the introduction of neutral salts complicates the problem considerably.

It is the purpose of this paper to attempt to establish the activity relation free from any such complicating influences as those mentioned above. A reaction apparently ideal in this respect is the conversion of acetyl-chloramino-benzene to p-chloracetanilide, catalyzed by hydrochloric acid. This reaction was first studied in aqueous solution, from a dynamic standpoint, by Rivett (Z. physik. Chem. 82, 201 (1913)). He determined the velocity constants of the conversion at 25° C. for concentrations of hydrochloric acid varying from 0.1 to 1.0 m. This reaction is catalyzed by the simultaneous presence of the hydrogen and chlorine ions, but, as shown by Rivett, the velocity is not proportional to the product of the concentrations of these ions, as calculated from conductivity measurements, the deviation being over 30% in the range studied.

This reaction is particularly adaptable to study from the activity standpoint. Since both the hydrogen and chlorine ions enter into the catalysis, it should be the product of the activities of these ions which determines the velocity at any temperature. This activity product can be calculated, as

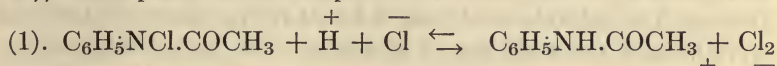
shown below, from electromotive force measurements of the cells:—



with thermodynamic accuracy, without liquid junction potential difficulties. This reaction, also, appears to be free from complications of the water molecule.

1. *The reaction Acetyl-Chloramino-Benzene \rightarrow P-Chloracetanilide.*

This reaction, according to the investigations of Orton and Jones (Report British Asso. for Advancement of Science (1910) 85), takes place in two steps.



They have shown that, in carbontetrachloride solutions, in the case of anilides which do not chlorinate, the reaction



is quantitative. (The chlorine was determined by the aspiration method).

Reaction (1) above is a measurably slow reaction, while reaction (2) is very rapid, so that the system approximates a continuous series of successive equilibria, with the concentration of the hydrochloric acid remaining practically constant.

If equation (7), derived above,

$$V = k a_A \times a_B \times a_C$$

is applicable to this reaction, the velocity should be proportional to the product of the activities of the acetyl-chloramino-benzene, the hydrogen ion and the chlorine ion:—

$$V = K_T a_A \times a_H \times a_{\text{Cl}}$$

in which a_A is the activity of the chloramine. Since the concentration of the hydrochloric acid remains constant, $a_H \times a_{\text{Cl}}$ is also constant; and we can write:—

$$V = k a_A \dots \dots \dots (8)$$

If the activity coefficient of the chloramine is proportional to its concentration throughout the reaction, then k should correspond to a first order reaction constant. Since the concentration

of the compound does not exceed 0.02 M, such an assumption is justified. The value of k should be given by the equation

$$k = K_T \times a_H \times a_{Cl}$$

where K_T is constant at any temperature, or

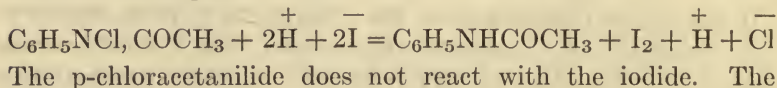
$$K_T = \frac{k}{a_H \times a_{Cl}} \dots\dots\dots (9)$$

2. Experimental:—

The values of the unimolecular velocity constant k , for the reaction acetyl-chloramino-benzene to p-chloracetanilide, have been determined at 17.65°, 25° and 35° C., for concentrations of hydrochloric acid from 0.1 to 1.0 M.; all concentrations were in mols per 1000 grams of water. The acetyl-chloramino-benzene was prepared by the method of Slossin (Ber. Deut. Chem. Ges. 28, 3265 (1895)) and was purified by recrystallization. The hydrochloric acid used throughout was made by diluting constant boiling acid, and its concentrations was checked by gravimetric analysis.

The procedure was similar to that used by Rivett. A hot saturated aqueous solution of the compound was prepared, and after standing for some hours was filtered. A weighed quantity of this solution was cooled slightly below the temperature at which the reaction was to be carried out, and a sufficient weight of the standardized acid added to bring the concentration to the required molality. It is important to note that a considerable rise in temperature, amounting to a degree in some cases, may take place upon mixing. The temperature was always adjusted before a zero reading was taken. The thermostat was regulated to - .02° C. A careful regulation of the temperature is essential, since a change of 0.1° C. causes a change of about 2% in the velocity constant.

The course of the reaction was followed by removing 25 c.c. of the solution in a pipette, at definite time intervals, and introducing it into a solution of potassium iodide. The following reaction takes place:—



free iodine liberated was titrated with a dilute (.015 M.) solution of sodium thiosulphate, using starch as an indicator. The value of k was calculated from the usual first order equation:—

$$k = \frac{1}{t} \log \frac{A_0}{A_1}$$

in which A_0 is the zero titer and A_1 the titer after “ t ” minutes. Readings were taken at such time intervals that six to ten titers could be made before the reaction reached the half-way point. These time intervals, naturally, varied greatly, depending on the temperature and concentration of acid. At 18° C. for 0.1 M. acid, readings were taken every two hours; while at 35° C., for 1.0 M. acid, it was necessary to make them every thirty seconds.

In Table No. 1 are given the final mean values of k for each concentration of acid; the maximum variation in a series was 1%. The concentration of acid (c) is given in mols per 1000 grs. of water.

TABLE 1
OBSERVED VELOCITY CONSTANTS*

17.65°		25.00°		35.00°	
C	K	C	k	C	k
0.1	0.0002160	0.1	0.000467	0.1	0.001500
0.2	0.000781	0.2	0.001718	0.2	0.00562
0.3	0.001710	0.3	0.003756	0.3	0.01200
0.4	0.003040	0.4	0.00666	0.4	0.02070
0.5	0.00472	0.5	0.01040	0.5	0.03254
0.6	0.00694	0.6	0.01505	0.6	0.0473
0.7	0.00952	0.7	0.02104	0.7	0.0645
0.8	0.01276	0.8	0.02800	0.8	0.0868
0.9	0.1660	0.9	0.0366	0.9	0.1126
		1.0	0.0465	1.0	0.1431

* NOTE:—The data by Rivett (loc. cit.), at 25° C. were determined on a volume normal basis, at odd concentrations. When corrected to weight molal they correspond fairly well to the values given above.

3. The Activity Values:—

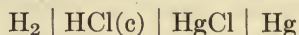
Activity has been defined above by the equation:—

$$F = RT \ln a + i \quad (\text{per mol})$$

or in general:—

$$F_1 - F_2 = RT \ln \frac{a_1}{a_2}$$

in which R is the gas constant, $(F_1 - F_2)$ the decrease in free energy of a system resulting from the transfer of one mol of the substance, or ion, from a concentration in which its activity is " a_1 ", to a concentration in which its activity is " a_2 ," at the absolute temperature T . The free energy change, $(F_1 - F_2)$ or $(-\Delta F)$ for a solution of hydrochloric acid in going from a concentration C_1 to C_2 can be determined by measurements of the electromotive force of the cells:—



at concentrations C_1 and C_2 . The difference in electromotive forces at these two concentrations, multiplied by the Faraday, gives the free energy change directly in joules.

Ellis (Jour. Amer. Chem. Soc. 38, 737 (1916) and 39, 2532 (1916) has accurately determined these free energy changes for hydrochloric acid at 18° , 25° and 35° C., over a large range of concentrations.

From the equation:—

$$\Delta F = RT \ln \frac{a_{\text{H}}^1 a_{\text{Cl}}^1}{a_{\text{H}}'' a_{\text{Cl}}''}$$

the ratio of the products of the ion activities can be calculated. Calling F_{H} and F_{Cl} the activity coefficients of the hydrogen and chlorine ions, respectively, then

$$(F_{\text{H}} \times C) \times (F_{\text{Cl}} \times C) = a_{\text{H}} \times a_{\text{Cl}}$$

in which C is the concentration of the acid. The value $\sqrt{F_{\text{H}} \times F_{\text{Cl}}}$ denoted by F_{a} , is the activity coefficient of the acid.

Ellis assumes this activity coefficient for hydrochloric acid to equal the conductance ratio at .001 M., having a value at this concentration of 0.985. He calculates from this the values of the activity coefficient for the higher concentrations.

The activity coefficients used in this paper were not taken directly from a plot of Ellis's data, but were calculated by a method suggested by Harned (Journ. Amer. Soc. 44, 252 (1922))

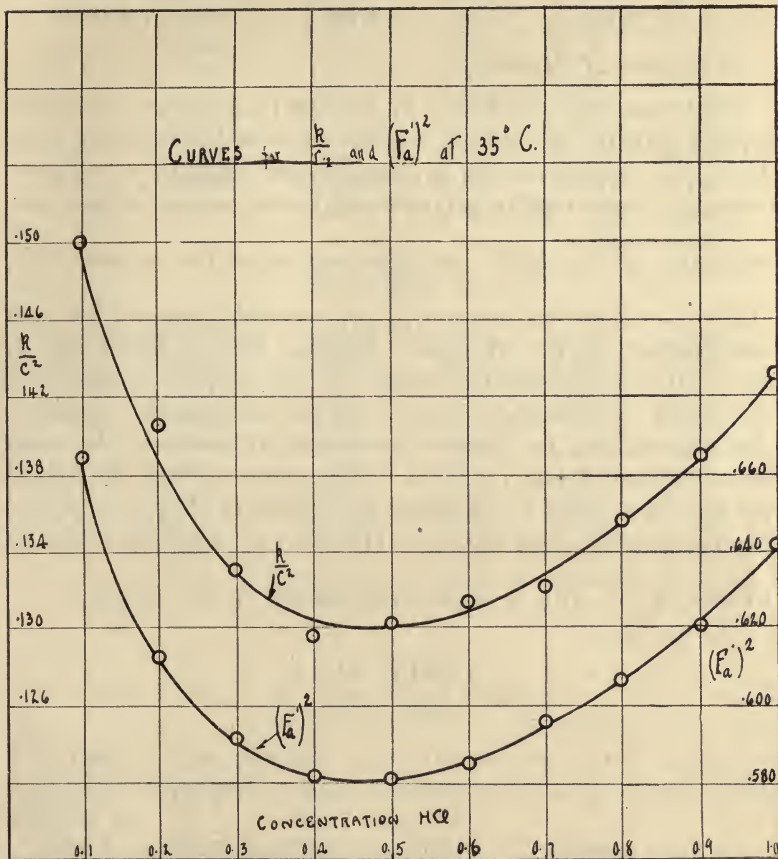


Fig. 1

from the equation:—

$$\log F_a^1 = \alpha^1 C - \beta^1 C^{m^1} \dots \dots \dots (10)$$

in which α^1, β^1 and m^1 are constants at any temperature, and C is the concentration of the acid. The values of these constants were determined graphically to give the best mean values of Ellis's results. They are:—

	18°	25°	35°
α^1	0.200	0.200	0.180
β^1	0.285	0.286	0.277
m^1	0.455	0.434	0.414

4. Discussion of Results:—

The values of k (Table No. 1), at each temperature, increased rapidly with the increase in concentration of hydrochloric acid. As a first approximation it was noticed that these velocity constants were roughly proportional to the square of the concentration of the acid. An examination of the values of $\frac{k}{C^2}$ (Table No. 2) shows, however, a pronounced minimum for each temperature, at 0.5 M. acid. Column No. 4, Table No. 2, shows the corresponding values of the activity coefficients, calculated as described above. It is immediately apparent that the minima for these values occur at precisely the same concentration, namely 0.5 M. This point is well illustrated by the curve (Fig. 1), in which the values of $(F_a^1)^2$ are plotted against concentration of acid. The form of the curve is similar to that of $\frac{k}{C^2}$, with a perfect coincidence of the minima.

TABLE NO. 2

Temp. 17.65° C.					
(1)	(2)	(3)	(4)	(5)	(6)
C	k	$\frac{K}{C^2}$	F_a^1	$(F_a^1)^2$	$\frac{K}{(F_a^1 \times C)^2}$
0.1	0.0002160	0.0216	0.832	0.692	0.0314
0.2	0.000781	0.01953	0.800	0.640	0.0311
0.3	0.001710	0.01900	0.785	0.617	0.0308
0.4	0.003040	0.01900	0.781	0.610	0.0313
0.5	0.00472	0.01888	0.780	0.608	0.0311
0.6	0.00694	0.01928	0.783	0.614	0.0314
0.7	0.00952	0.01940	0.790	0.624	0.0313
0.8	0.01276	0.01990	0.799	0.639	0.0314
0.9	0.1660	0.02050	0.810	0.655	0.0310

Mean 0.0312

Temp. 25.00° C

0.1	0.000467	0.0467	0.822	0.605	0.0692
0.2	0.001718	0.0430	0.790	0.623	0.0690
0.3	0.003756	0.04175	0.777	0.604	0.0691
0.4	0.00666	0.0416	0.773	0.598	0.0695
0.5	0.01040	0.0416	0.773	0.598	0.0695
0.6	0.01505	0.0418	0.778	0.605	0.0692
0.7	0.02104	0.04295	0.785	0.616	0.0697
0.8	0.02800	0.0438	0.795	0.632	0.0693
0.9	0.03660	0.0448	0.807	0.651	0.0694
1.0	0.0465	0.0465	0.820	0.762	0.0692

Mean 0.0693

Temp. 35.00° C

0.1	0.001500	0.1500	0.815	0.664	0.226
0.2	0.00562	0.1405	0.783	0.613	0.229
0.3	0.01200	0.1333	0.769	0.591	0.226
0.4	0.02070	0.1294	0.763	0.582	0.223
0.5	0.03254	0.1302	0.762	0.581	0.224
0.6	0.0473	0.1315	0.765	0.585	0.225
0.7	0.0645	0.1317	0.771	0.594	0.222
0.8	0.0868	0.1358	0.779	0.606	0.224
0.9	0.1126	0.1390	0.788	0.620	0.224
1.0	0.1431	0.1431	0.800	0.640	0.224

Mean 0.224

In Column No. 6 are given final values of $\frac{k}{(F_a^1 \times C)^2}$. The constancy of these figures, at each temperature, over the entire range of concentration, is well within the limit of experimental error.

Since, by definition of F_a^1 :— $(F_a^1 \times C)^2 = a_H \times a_{Cl}$
the relation $K_T = \frac{k}{a_H \times a_{Cl}}$ is without any question substantiated. This conclusion is particularly significant in this case, when we consider that these results are based entirely on accurate thermodynamic activity data, without complications due to liquid junction potentials, and without any assumptions as to individual ion activities.

5. The Temperature Coefficient.

With the development of the radiation hypothesis of reaction velocity, it is of considerable importance to obtain the temperature coefficients of reaction velocity constants. The temperature coefficient should be expressed by an equation of the form

$$\frac{d \ln K_T}{dT} = \frac{E_c}{RT^2} \dots \dots \dots (11)$$

where E_c may be called the critical increment. According to the rule of Arrhenius E is a constant. It is not necessary to mention the various meanings attached to E by different authors (W. C. McC. Lewis, *System of Physical Chemistry*, Longmans; Perrin, *Annales de Physique*, Ser. 9, 11, 5 (1919); Tolman (*Jour. Amer. Chem. Soc.* 42, 2506 (1920) and others), but it is of some value to point out that in this case the rule of Arrhenius is not valid over the short range of temperature. The plot of $\ln K_T$ against $1/T$ is not a straight line but has considerable curvature, showing that E_c varies considerably with the temperature. Integration of (6) between temperature limits T_1 and T_2 , assuming that E_c is constant, gives

$$E_c = \frac{4.571 T_1 T_2}{T_1 - T_2} \log \frac{K_{T_1}}{K_{T_2}} \dots \dots \dots (12)$$

whence E_c is found to be $1.356 \times 10_5$ Cals. between 25° and 35° C., and 1.196×10 Cals. between 17.65° and 25° C. This is sufficient to show that the rule of Arrhenius does not hold.

The Neutral Salt Effect.

From measurements of the electromotive forces of cells of the type



it is possible to obtain the product of the activities of the hydrogen and chlorine ions in acid salt mixtures exactly, without any difficulties arising from liquid junction potentials. Exact measurements of these cells have been made by Harned (*Jour. Am. Chem. Soc.* 38, 1986 (1916); 42, 1808 (1920),) so that the

required thermodynamic data are available for applying the activity theory to the velocity of conversion of acetyl-chloramino-benzene to p-chloracetanilide. Velocity measurements on this reaction have been made, using hydrochloric-sodium chloride mixtures, and hydrochloric acid-potassium chloride mixtures

which show that the relation $K_T = \frac{k}{a_H \times a_{Cl}}$ which holds so beautifully for hydrochloric acid alone fails to hold in the presence of the neutral salts. K_T instead of remaining constant, decreases considerably with increasing salt concentration. This study will be the subject of a future communication.

Summary:—

1. It has been derived, from thermodynamic considerations, that, in reactions in liquid systems catalyzed by specific ions, it is the activities of such ions which determine the velocity of the reaction at any temperature when the catalysis depends on successive states of equilibria.

2. The velocity constants of the reaction acetyl-chloramino-benzene to p-chloracetanilide, catalyzed by hydrochloric acid, have been determined at 17.65°, 25° and 35° C. for concentrations of acid from 0.1 to 1.0 M.

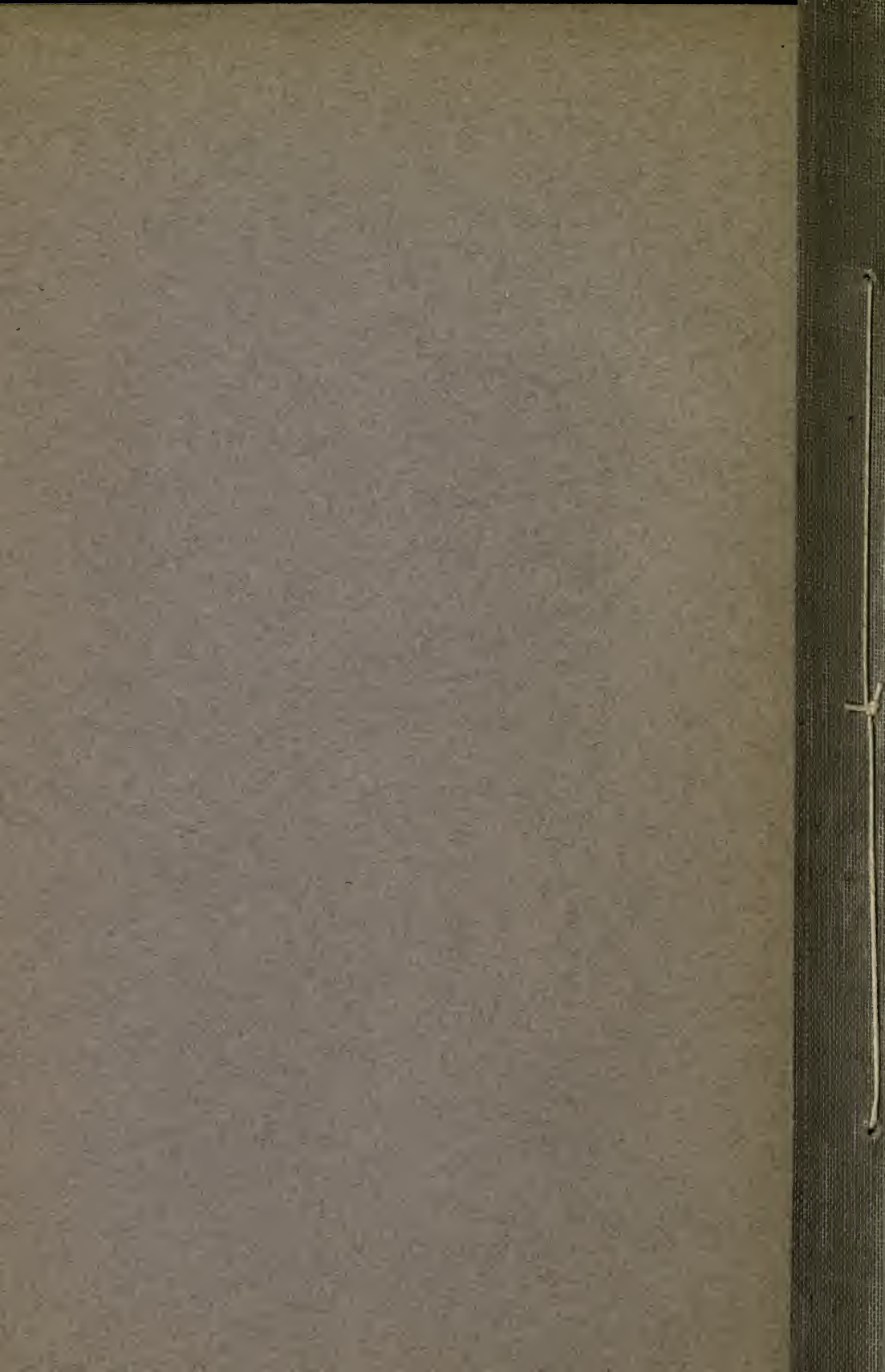
3. It has been shown that these velocity constants at each temperatures are proportional to the product of the activities of the hydrogen and chlorine ions of the catalyzing acid.

4. As far as we are aware, this is the first case in which homogeneous catalysis may be calculated with exactness over a wide concentration range and in concentrated solutions, without guess work concerning liquid junction potentials.

5. The temperature coefficient has been considered and the critical increment has been roughly calculated and shown to vary considerably with rise on temperature.

6. The relation $K_T = \frac{k}{a_H \times a_{Cl}}$ which holds exactly for solutions of hydrochloric alone, fails to hold when acid-salt mixtures are used as catalysts.

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